

PROCEEDINGS
OF THE
NATIONAL ACADEMY OF SCIENCES
INDIA
1949

PART II]

SECTION A

[VOL. 18

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ALLAHABAD

PUBLISHED BY THE COUNCIL

Price Rs. 5 (India) : Rs. 5/8 (Foreign)

Corrigendum slip of Part 2, Section A, Vol. 18, 1949

CORRIGENDUM

In my paper, "Determination of Elastic Constants of gels by Ultrasonic Method," the rise of amplitude after the second minima is due to the transmission of sonic energy directly. At angles greater than 70° this direct transmission starts taking place. Figures 4-7 needed this explanation.

ARVIND MOHAN SRIVASTAVA

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[VOL. 18

**DETERMINATION OF ELASTIC CONSTANTS OF GELS
BY ULTRASONIC METHOD**

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(Received on September 8, 1949)

Abstract

The ultrasonic pulse technique developed herein is applied to the determination of the elastic moduli of four gels. The method is entirely new to this line of work and recommends itself because the determinations are quick, accurate and the sample is left undamaged after experimentation. The theories of gel formation have been analysed in brief and attempts are being made to co-relate them with the elastic data obtained.

1. INTRODUCTION

Considerable interest has been shown in the determination of the elastic constants of plastics and other high polymers during the recent years. There is, however, a paucity of published data in the case of gelatinous substances. The importance of this work is three-fold, viz., (1) it provides a basis for comparison, (2) they furnish a scientific criterion for studying the semi-solid nature of gels, and (3) they afford to provide a basis to understand the ultimate mechanical properties of gels.

W. T. Richards¹ and Reggiani² have studied the properties of some hydrosols prepared by emulsification. Marinesco³ has considered the effect of sound waves on gels. He has, however, only considered the absorption of waves and the gradual diminution of the ampli-

tude of plane waves. A year later he used an expression⁴ to inter-relate the velocity with compressibility and density of the medium in which the plane waves propagate. Bez-Bardili⁵ determines the velocity of sound waves in solids and relates them to their elastic constants. These attempts make it apparent that the importance of ultrasonic methods have been under-rated by the colloid chemists. In this paper it is, therefore, intended to initiate the supply of data that might enable them to look into the problem from a totally neglected angle.

2. EQUIPMENT

The experimental method is an adaptation of the pulse technique which has been described by Pellam and Galt⁷ and by Teetar⁸ originating in the work of Massachusetts Institute of Technology Radiation Laboratories. The complete equipment consists of four parts (units) linked together as shown in the schematic diagram, Figure 1.

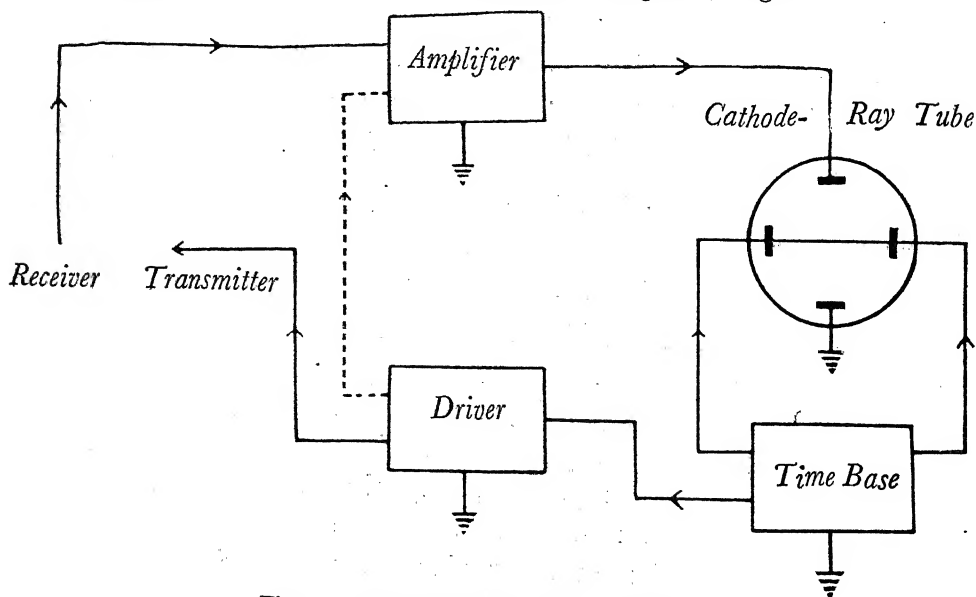


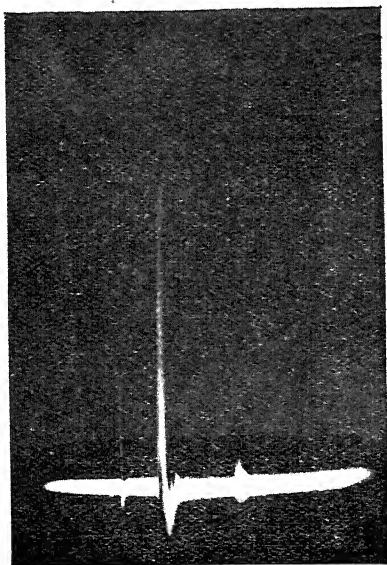
Fig. 1. Block diagram of the equipment.

The Time Base controlled by the alternating current supply mains triggers the Driver unit which supplies electrical impulses to the Transmitter. Thus the equipment operating from a normal 50 cycles per second A. C. mains transmits 50 pulses per second. We now

proceed to consider the transmission of a single pulse at 2.5 Megacycles per second.

The Time Base applies a rapidly changing potential to the X plates of the cathode ray tube so that the cathode ray tube spot moves at a constant velocity across the screen from left to right. Just after the start of the time-base stroke the Driver Unit is triggered by the former and applies a short pulse of energy at the desired frequency of 2.5 Mc/sec. to the Quartz Transmitter; a fraction of this energy is fed directly to the Y plates of the cathode ray tube. Thus the spot moving from left to right across the screen is deflected vertically at the instant of transmission.

Electrical energy supplied to the transmitter is converted into a pulse of 2.5 Mc/sec. supersonic energy which is propagated through the sample under observation, reconverted into electrical energy by the receiver, and this transmitted energy is applied to the Y plates



Photograph 1. Showing the transmitted pulse amplitude.

of the cathode ray tube. The spot is therefore, deflected vertically again. The velocity of the spot as it moves across the cathode ray tube screen from left to right is adjusted so that the vertical deflection occurs

at the right side of the trace. The two vertical deflections are shown in photograph 1.

Conversion of electrical energy to supersonic and vice-versa is affected by the piezo-electric action of a 2 centimetre diameter, 2.5 Mc/sec., X-cut quartz disc fixed to the ends of two cable heads or ends. Both the sides of these quartz discs are thinly silver plated;

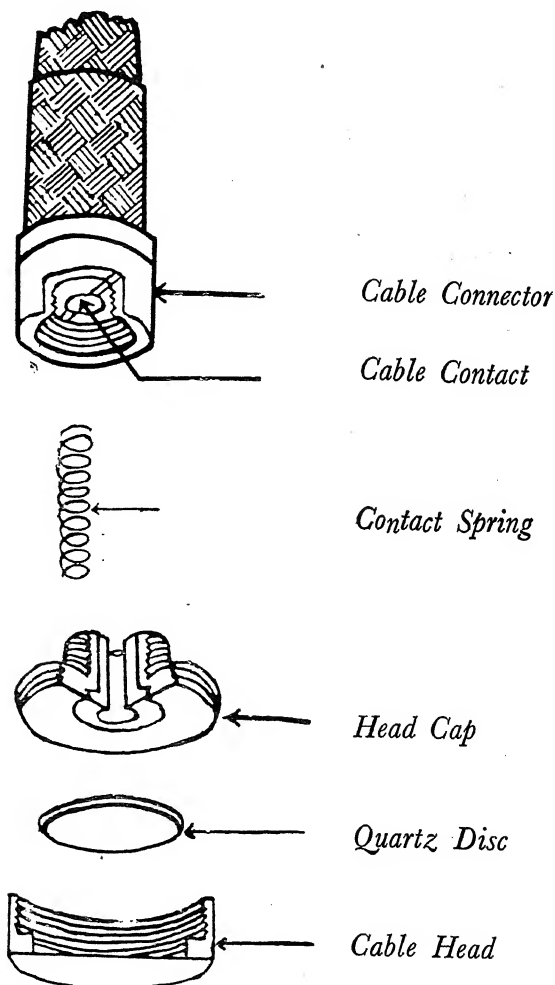


Fig. 2. The assembly and housing of quartz crystal.

contact between the upper surface of the disc and the central conductor of the cable is affected by a spring located in the head cap. The

heads each complete with a quartz disc, head-caps and contact springs are attached to the co-axial concentric cables. Care is taken to ensure that the contact springs are free to slide in the head-caps, and that they press firmly against the recessed cable contacts. A detailed sketch of the whole assembly is seen in Figure 2.

A key is used with which the head-cap may be removed in case it be necessary to examine or replace the quartz disc. The quartz disc and the inner surface of the head should be clean and free from grit. After supplying two or three drops of light machine oil to the inner side of the head the quartz disc is inserted and pressed lightly into position; the head-cap is screwed tightly into position; and the contact spring replaced.

In the apparatus a frequency selection switch is provided on the right side of the panel in front. This selects the output frequency of the transmitter. It consists of the multiway switch introducing various inductances in parallel with the capacity of the transmitter lead (earth) and the crystal. The available frequencies are 2.5 Mc./sec. 2.25 Mc./sec., 1.25 Mc./sec., and .625. Mc./sec. , and X (mixed frequency). In each inductance there is an adjustable core which requires adjusting if the length of the transmitter lead is changed for any purpose, but otherwise should never be changed.

It is not advisable to lay down rigid rules for the selection of appropriate frequency for any given application, as experience has always appeared to be the best guide. The type of the material often is the determining factor, as for example 2.5 Mc./sec. is suitable for most steels, while for copper this would be too highly attenuated. In the latter case .625 Mc./sec. is more suitable. The position X allows a mixed frequency to be generated and the highest which will penetrate the material in question and can thus be directly seen on the cathode ray tube screen.

Surface conditions of the test sample should be as good as practice will allow, but difficulty arises in case of gelatinous substances which are unrigid and uneven. If there is insufficient sensitivity for this reason the amplifier sensitivity can be sufficiently increased by inserting a plug-in filter in parallel with the receiver.

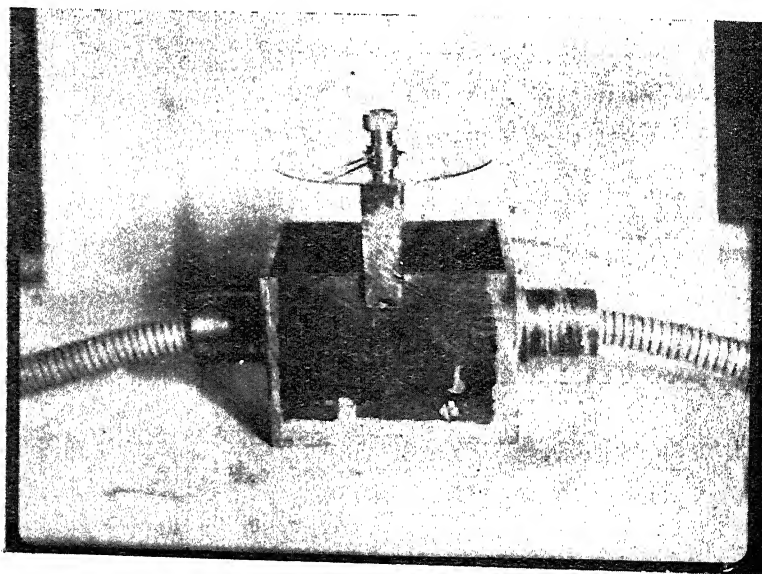
The frequency of this plug-in filter is the same as that of the transmitter.

The two techniques available have been suggested by Bar and Walti⁴ and by Bez-Bardili⁵. The mechanical wave set up by the quartz is impinged upon a slab of the material held normal to the direction of propagation of the wave and the energy transmitted is detected by the receiver quartz diametrically opposite to the previous one. The generator, the sample of gel and the detector are immersed in a liquid bath to avoid the extreme mismatch of acoustic impedance at the solid-gas interface.

While the two quartz are kept fixed in the two slots in the two opposite walls of the liquid container (photograph 2), the test sample of the gel can be rotated in a vertical plane, changing the angle of incidence of ultrasonic waves on the slab. This angle of rotation can be measured on a graduated disc over which a pointer moves.

3. THEORY AND TECHNIQUE

In any isotropic media two types of deformations are exhibited on the application of a stress. These are the two well known states of



Photograph 2. Showing the experimental cell.

extension and shear. The Young's modulus E expresses a resistance to tension and shear modulus S expresses the resistance to shear. In the first type of deformations σ , the Poisson's ratio is a constant ratio of the cross-sectional contraction to the elongation in length. A relation between these three is given by,

$$E = 2(1 + \sigma) S. \quad (1)$$

Sound waves that are propagated in a solid take up two velocities depending upon the two deformations associated with them. The waves in the case of a simple shear are called shear, transverse or rotational ones and their velocity is given by,

$$V_s = \sqrt{\left(\frac{S}{\rho}\right)} \quad (2)$$

where ρ is the density of the gel. In the deformations of an extension the vibrations are called dilatation, longitudinal or irrotational and their velocity is given by,

$$V_e = \sqrt{\left(\frac{(1 - \sigma) E}{\rho(1 + \sigma)(1 - 2\sigma)}\right)} \quad (3)$$

also,

$$\sigma = \frac{k^2 - 2}{2(k^2 - 1)} \quad (4)$$

where,

$$k = V_e/V_s. \quad (5)$$

Thus a knowledge of V_e and V_s enables us a determination of σ , E and S . From these one can determine the compressibility, m . The Bulk modulus of elasticity is,

$$K = \frac{E}{3(1 - 2\sigma)} \quad (6)$$

and knowing that $m = \frac{1}{K}$ we can calculate m .

The method used herein is based upon the variation of the amplitude of the transmitted energy with the angle of incidence of the ultrasonic beam on the slab of jelly. Since the velocity in

solid is greater than that in the liquid the wave-trains are refracted away from the normal and the indices of refraction for the two waves are,

$$\left. \begin{aligned} n_i &= \frac{\sin \theta}{\sin \theta_i} = \frac{V_x}{V_i} \\ n_s &= \frac{\sin \theta}{\sin \theta_s} = \frac{V_x}{V_s} \end{aligned} \right\} \quad (7)$$

where V_x is the velocity in the tank liquid.

As θ increases θ_i also increases so that at a value θ_i of θ , $\theta_i = 90^\circ$, the dilatation waves are totally reflected and there is a pronounced minimum in the intensity as well as the amplitude of the transmitted

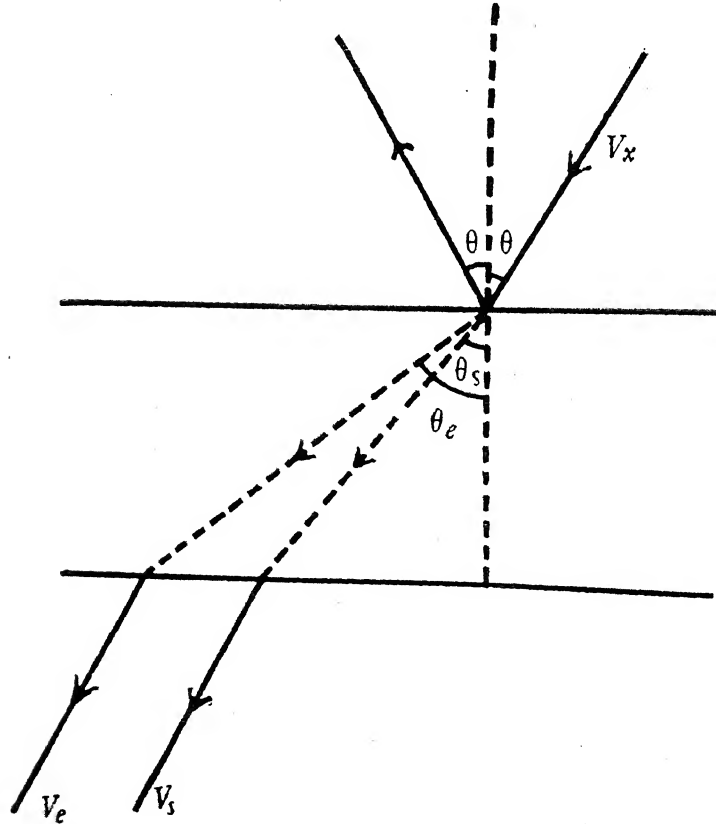


Fig. 3. Showing the various wavetrains.

energy. As θ goes to a further value θ_2 , $\theta_2 = 90^\circ$ and the shear waves are totally reflected, then at θ_1 and θ_2 ;

$$\left. \begin{aligned} V_1 &= V_2 / \sin \theta_1 \\ V_2 &= V_1 / \sin \theta_2 \end{aligned} \right\} \quad (8)$$

The amplitudes of the transmitted wave are shown in photograph for a single gel at an angle of incidence other than that at the critical angle. The first vertical maxima shows the start of the pulse, the second and largest amplitude is the magnitude of the transmitted wave and the third maxima to the extreme right is due to reflection of the wave from the front and back surfaces before detection. On rotating the slab of gel the second maxima diminishes twice as the two wave-trains are totally reflected respectively

The above technique has been adopted in my work because of several definite reasons, the main being that; no extensive preparation of the gel sample is needed, the sample thickness is immaterial, the sample is not damaged during the process, evaluations are simple easy and accurate and no involved calculations are necessary.

4. RESULTS

To test the accuracy of the method a few determinations were made with substances whose elastic constants are well known. The results so obtained show that the method is quite safe for application and the accuracy is quite satisfactory. Table 1 shows the values of the angles observed and the velocities of the two wave trains computed therefrom. Figs. 4 to 7 indicate the angles observed when the total reflection of the waves occurs. The two dips correspond to the values θ_1 and θ_2 . Table 2, gives the values of the Poisson's ratio, the refractive indices and the ratio k . The third table presents the elastic constants for the four gels that have been studied here.

For the purposes of these calculations the velocity of waves in the tank-liquid water, is taken to be $1.55 \cdot 10^5$ cms./sec. All the values of the velocity are expressed in centimetres per second. Values of E and S are given in dynes per square centimetre, that of m is given in reciprocal of the above.

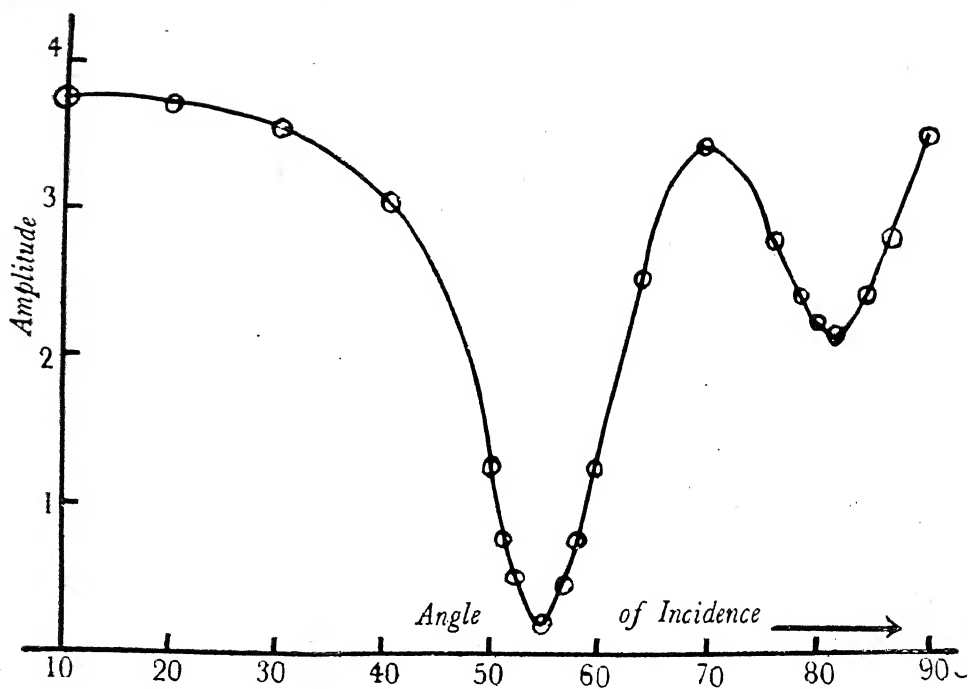


Fig. 4. Showing the variation of amplitude of transmitted wave in Silica Gel.

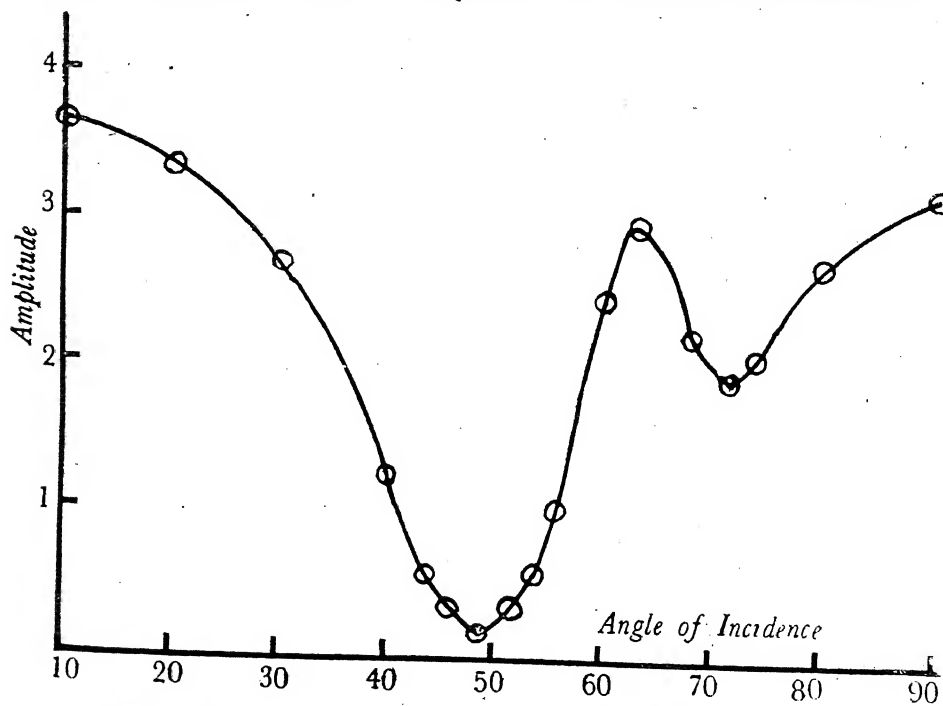


Fig. 5. Showing the variation of amplitude of transmitted wave in Barium Sulphate Gel.

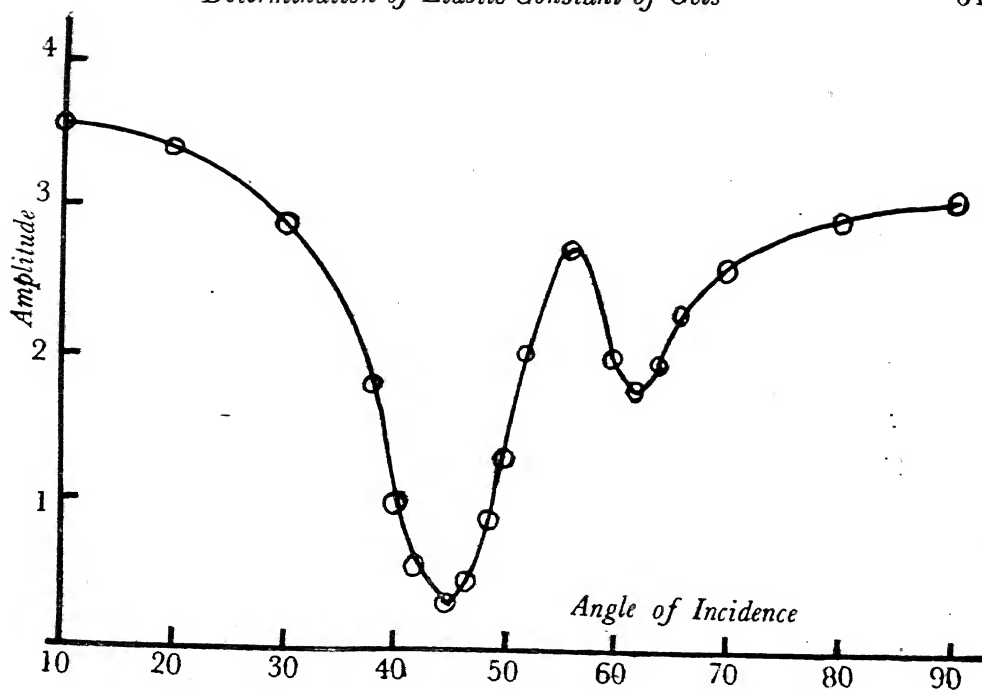


Fig. 6. Showing the variation of amplitude of transmitted wave in Iron Silicate Gel 1.

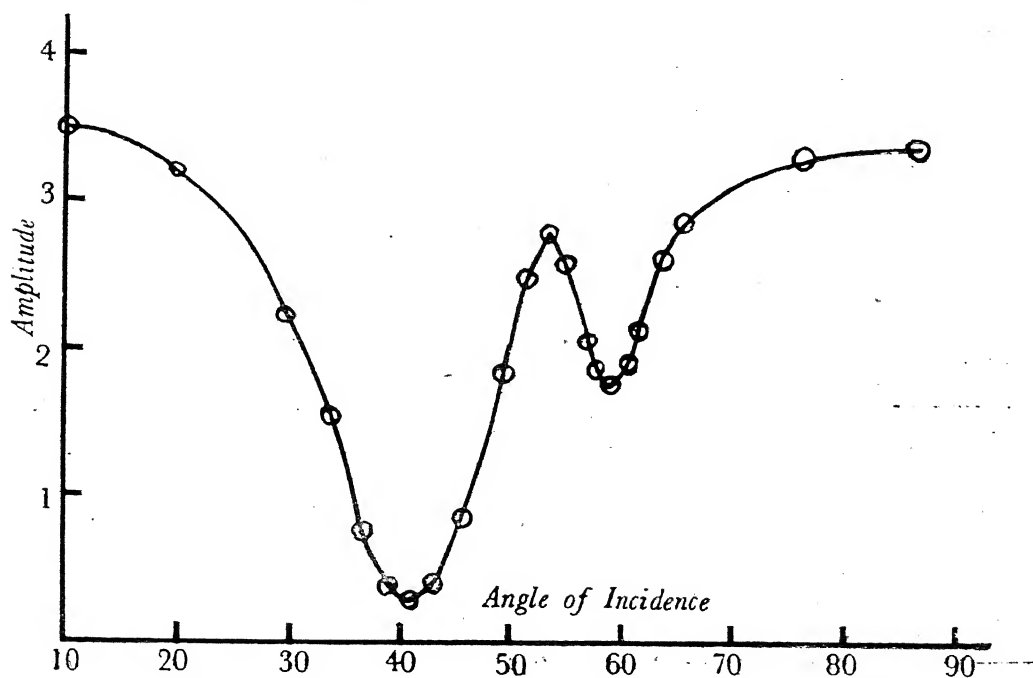


Fig. 7. Showing the variation of amplitude of transmitted wave in Iron Silicate Gel. 2.

Table No. 1.

No.	Gel	ρ	θ_i	θ_s	Ve	Vs
1.	Silica, SiO_2	1.14	53.5°	81.0°	$1.85.10^5$	$1.57.10^5$
2.	Barium Sulphate	1.22	49.0°	72.0°	$2.06.10^5$	$1.65.10^5$
3.	Iron Silicate 1.	1.27	45.0°	62.0°	$2.15.10^5$	$1.70.10^5$
4.	Iron Silicate 2.	1.35	41.0°	59.0°	$2.25.10^5$	$1.74.10^5$

Table No. 2.

No.	Gel	n_i	n_s	k	$-\sigma$
1.	Silica, SiO_2	.81	.98	1.19	.63
2.	Barium Sulphate	.74	.95	1.24	.44
3.	Iron Silicate 1	.69	.89	1.26	.35
4.	Iron Silicate 2	.66	.86	1.29	.22

Table No. 3.

No.	Gel	E	S	K	m
1.	Silica SiO_2	$2.01.10^{10}$	$2.84.10^{10}$	$2.93.10^9$	$3.41.10^{-10}$
2.	Barium Sulphate	$4.01.10^{10}$	$3.22.10^{10}$	$7.95.10^9$	$1.26.10^{-10}$
3.	Iron Silicate 1	$4.79.10^{10}$	$3.67.10^{10}$	$9.40.10^9$	$1.06.10^{-10}$
4.	Iron Silicate 2	$5.18.10^{10}$	$4.09.10^{10}$	$11.46.10^9$	$.88.10^{-10}$

5. DISCUSSION

The colloidal state of matter shows certain interesting and distinctive properties that are absent in the two constituent phases themselves. A gel represents a specific type of colloid wherein a liquid is dispersed in a solid dispersion medium. The properties of such a system are therefore naturally perplexing in certain respects. Although a large amount of work has been done on gels there is no agreed view on the mechanism of gel formation. Weimarn⁹ holds the view that a precipitate may be crystalline, amorphous, or gelatinous according to the percentage of supersaturation. Bradford¹⁰ is in general agreement with Weimarn and he maintains that the gels have two phases—an ultramicroscopic solid phase soaked in a liquid dispersion medium retained by capillary and molecular forces. Bancroft¹¹ on the contrary believes that there are other factors besides percentage supersaturation that effect the formation of the nuclei in the gels. It is apparent, therefore, that much further work is needed to elucidate the mechanism of gel formation to understand properly the semi-solid nature of these substances.

A large amount of work has been done by Dhar¹² who has classified the jellies into three groups. In the first group the particles show some basic network and the jellies are easily formed, more stable like gelatine, agar-agar, soaps, etc. The second group consists of gels formed by the slow coagulation of a sol throughout its entire mass and the particles do not consist of a network. Hydroxides of iron and chromium are members of this class. The substances involved in this class have a marked affinity for water and they are less stable. The third group forms the Weimarn class consisting of substances precipitated very suddenly, they are the least stable.

On accumulation of further data we intend to support one of the above views on the mechanism of gel formation. For the present this paper supplies a new approach to others interested in this line of work.

6. ACKNOWLEDGEMENT

I wish to record my sincerest thank to Prof. N. R. Dhar and Dr. R. N. Ghosh who have afforded me encouragement and guidance that enabled me to undertake this work.

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ACTION OF LIGHT ON COLOURING MATTERS AND THEIR OXIDATION

By

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Photo-oxidation and photo-decomposition of colouring matters.

In my book 'Chemical Action of Light' (Blackie & Sons. 1931) it was pointed out that the phenomenon of photo-oxidation of organic and inorganic substances by atmospheric oxygen is of common occurrence. In recent years we have carried on systematic work on the photo-oxidation of carbohydrates, celluloses, fats, glycerol, pentosans and other energy materials by air at the ordinary temperature in presence of soil or insoluble oxides, phosphates, sulphates, carbonates etc and have shown that in these oxidations of energy materials, fixation of atmospheric nitrogen takes place, more in light than in the dark. (Dhar. Presidential address, National Academy of Sciences, India. 1935, 1937. *Proc. National Academy of Sciences, India*. **15** (1946), 15. **16**, (1947), 6.)

Dhar and co-workers (*Z. anorg. Chem.* **142**, (1925) 299) have shown that dyes are solutions or suspensions of unstable substances and can be oxidised or reduced. Usually these solutions or suspensions when exposed to light are oxidised by the dissolved oxygen and hence there is a bleaching of the dye on exposure to light. In presence of strong light, specially ultra-violet radiations, some dye solutions or suspensions are actually decomposed and lose colour, just as solutions of ammonium nitrite, potassium persulphate, trichlor-acetic acid etc., are decomposed in light. Even when the dyes are adsorbed on fibres photo-reduction of the dyes by cellulose can take place. Moreover some dyes adsorbed on cellulose also undergo photo-oxidation on the cellulose surface by air.

Most of the dyes do not fade in absence of air and fibre. Wool and silk are found to exert less reducing action on dyes than cotton.

It is well known that substances like ozone, hydrogen peroxide, ammonium nitrite etc undergo thermal and photo-chemical decomposition readily. Similarly explosives which are very unstable substances can also undergo decomposition by increase of temperature or when exposed to light. Dyes like picric acid and Aurantia behave like explosives and fade due chiefly to the breaking of the molecules by light absorption.

On the other hand, most of the basic dyes are free from oxygen and contain several carbon and hydrogen atoms in the molecule and they can behave as reducing agents specially in presence of light. Such dyes can undergo photo-oxidation by the oxygen of the air and get bleached. The basic dyes are less fast to light than acidic dyes which are certainly less reducing in their properties than basic dyes. All basic dyes contain less oxygen in their molecules than acidic dyes. It is generally observed that the presence of unsaturated and conjugate groups is needed for the formation of a dye. But these groups also make the molecules unstable. Moreover, it is well known that the greater the molecular weight of a dye and the greater the number of unsaturated and conjugate groups present, the greater is the depth of its colour. Also the dyes with low molecular weight exist in the molecular condition in solution and are more easily photo-oxidised by air than dyes with larger molecular weights which are either insoluble in water or form colloids and are less liable to be photo-oxidised. It is clear, therefore, that a dye can fade due to the one or more of the following causes:—

(1) Photo-decomposition. (2) Photo-oxidation by air. (3) Photo-reduction by the fibre or mordant.

It appears that with basic dyes photo-oxidation by air is the chief cause of fading. But with acidic dyes containing oxygen atoms in the molecule there is a greater possibility of photo decomposition and photo-reduction than photo-oxidation.

In some cases dyes containing oxygen can undergo decomposition in light by auto-oxidation and reduction just like nitrous acid or benzaldehyde according to the equations:—



It is interesting to note that the use of the nitro compounds picric acid and Aurantia containing three and six nitro groups in the benzene nucleus, as dyes has been given up because they are fugitive but they are used as explosives. Aurantia is used as a staining material. Many years ago D. Berthelot and H. Gaudechon [Compt. rend. **153**, 1220. (1911); **154**, 201, 514. (1912)] studied the photo-decomposition of explosives like powders, cordite, nitro-glycerine etc. in amounts weighing from 0.24 to 0.45 gram and observed their rapid decomposition to gaseous products when exposed to ultra-violet radiations. Such decomposition also takes place in visible light at a lower speed. It appears, therefore, that organic compounds and dyes containing several nitro groups in the molecule may undergo photo decomposition and may prove fugitive. Moreover such dyes containing several oxygen atoms in the molecule may also undergo photo-reduction by the fibres or mordants which are generally reducing agents, specially cotton, which in presence of light exerts more reducing property than wool or silk. Hence dyes with several nitro groups are not likely to be commercially successful because of their fugitiveness and instability.

It is generally believed that in photosynthesis in plants the following compounds according to their increasing complexity and molecular weight are produced:—

Formaldehyde—glucose—complex sugars—starch—cellulose—lignin.

Formaldehyde, glucose, cane sugar, starch etc. have been found to decompose in light specially ultra-violet, into different gaseous products in absence of oxygen. Dhar and coworkers (Influence of light on some biochemical processes. 1935) have shown that all carbohydrates, fats, organic acids, cellulose and even lignin can undergo photo-oxidation by air and in many cases the nitrogen of the air is also fixed in this process. It appears therefore that organic compounds

can undergo photo-oxidation and photo decomposition specially under strong illumination. The ease of photo-oxidation and decomposition decreases markedly as the molecules become more and more complex. This behaviour is observable with natural and artificial colouring substances. Although they are organic substances and are liable to be photochemically oxidised and decomposed, they resist these processes pretty well because they are usually derivatives of aromatic hydrocarbons and their heterocyclic counterparts have a ring structure. More over, most dyes are of large molecular weights and are either insoluble in water or exist in the colloidal condition having large molecular aggregates. Once the colouring matter is adsorbed on the fibre with or without mordants they are usually stabilised perhaps by rendering them as insoluble as possible and forming stable adsorption complexes. In this connection it is interesting to note that the phospho-molybdo-tungstic acid lakes formed by adsorbing methyl violet and other basic and cyanin dyes make them more fast towards light. In other words, the greater the stability of the adsorption complex formed with mordants and fibres the greater is the stability towards light.

The natural colouring matter chlorophyll A and chlorophyll B containing a large number of carbon and hydrogen atoms and an atom of magnesium would behave as reducing substances like some of the basic dyes and would be liable to photo-oxidation by air. On the other hand, the anthocynin colouring substances notably pelargonidin, cyanidin, peonidin, delphinidin, malvidin, hirsutidin are richer in oxygen than chlorophyll and resist photo-oxidation by air better and are more fast to light than chlorophyll. Similarly the following dye stuffs quercetin, fisetin etc. have been in use as yellow mordant dyestuffs from ancient times. Quercetin is still a valuable dye for wool. Luteolin, another natural flavone dye is being used for producing a fast yellow shade on wool and silk with aluminium or tin mordants. These are more fast as they contain more oxygen than chlorophyll and hence resist photo-oxidation. It is interesting to note that the majority of colouring substances both natural and artificial contain nitrogen which makes the dyes more stable towards photo-oxidation.

Most basic dyes have lower molecular weights than acidic dyes. They contain less oxygen than acidic dyes and hence possess more reducing power and are thus liable to be photo chemically oxidised by air. Cotton being more reducing in its properties than wool or silk, the basic dyes have greater advantage over acidic ones in the dyeing of cotton.

Most of the azo dyes, both basic and acidic have smaller molecular weights than some other more complex dyes and the weak point of the azo dyes is their unstability towards light. By increasing the molecular weight of such azo dyes the light fastness increases. Certain groups such as the pyrazolone and nitro or sulphonic groups ortho to the azo links are beneficial to light fastness. Tartrazine, an acidic dye is a bright yellow compound exceedingly fast to light like all pyrazolone colours. Auramine hydrochloride, a basic dye, is one of the most important synthetic dyestuffs and contains no sulphur. As the molecular weight of this substance is not high (303.5), the shade is not fast to light. The well known nitro acidic dyestuff Naphthol yellow S having a molecular weight of 392, used in dyeing animal fibres changes colour to a brownish shade when exposed to light. Basic azo dyes such as Bismarck brown can be fixed on cotton mordanted with tannin and tartar emetic but this method is now of little importance. On the other hand many azo dyes having suitably disposed hydroxy or carboxy groups form inner coordination compounds with copper and chromium salts and these are of first importance. They frequently possess very high light fastness as well as good washing fitness. The thiazole acidic dye Primuline (molecular weight 475) and its diazo salts are not light fast.

The simpler basic dyes such as magenta and malachite green are readily bleached by sunlight which is a serious weakness of most of the triphenyl methane group of colouring matters. The molecular weight of magenta is 322.5 and that of malachite green is 364.5. On the other hand the alizarin cyanin dyestuffs such as alizarin cyanin green which is an acidic dye of molecular weight 578 are equal in purity of shade to the triphenyl methane colours and are very much faster to light. It is interesting to note that several triphenyl methane

dyes containing negative substituents are faster than the simpler basic dyes and some of the sulphonated triphenyl colours are of great beauty and are acid dyes suitable for colouring wool but not very light stable.

Some phenyl and toluidine derivatives of rosaniline have yielded well known basic dyes like Victor blue 4R, Night blue and these are mainly used for colouring silk. The shades are good but fugitive to light. The acid dyes obtained from Rosalic acid, aeriochrome azurol B dyes wool a wine red colour and the dye is moderately fast to light. The sulphonated Rhodamines like acid violet 4R or violamine R or violamine 3B are much faster to light than the basic rhodamines. They range in colour from violet to blue and are of considerable value for dyeing of wool or silk. Fluorescein dyes with low molecular weights, although acidic ones, are fugitive towards light. The halogenated fluoresceins are most beautiful artificial dyes but are not light fast. Rose Bengale and erythrosine are of value for sensitizing photographic plates to green and yellow light. These dyes are frequently mixed with the isocyanin dyes for improving their sensitivity towards light. When flavanthrone is treated with alkaline sodium hydrosulphite at 65° a violet blue colouring matter for dyeing cotton substantively is produced. When the dyed fibre is exposed to air the blue colour changes to brilliant yellow by oxidation but the colour is not fast to light. On the other hand, the acid dye Indanthrene golden orange G gives a purple shade on cotton which when oxidised becomes a light fast orange dye. It is interesting to note that the following colouring matters are being used as light filters and for absorbing radiations of different wave lengths in all kinds of optical work :—

Fluorescein, Rhodamine B, Nitroso-dimethylaniline, Triphenyl methane, Methyl violet, Methyl green, Picric acid, Crystal violet, Double green, Violet yellow, Aesculin, Guinea green B extra, Chrysoidine, Eosin, Tartrazine etc. On long exposure to light some of these dyes undergo photo-oxidation or decomposition.

In dyeing by the two famous colouring matters of the ancient world—Tyrian purple and Indigo—oxidation of the colouring matter

by air in presence of light played a very important part. If cotton is continuously exposed to sunlight, it loses strength due to partial oxidation. This is particularly true of curtains, which may appear in perfect condition when hanging at the windows but when taken down may fall apart in spots where sunlight has reached them.

The photo-decomposition of chlorophyll solution was probably first observed by Senebier in 1788. He noted that solutions of chlorophyll in acetone, alcohol, benzene and ether were rapidly decolourised by light in presence of air. Gaffron (Ber. 60 B, (1927) 2229) has shown that under the influence of light a solution of chlorophyll in acetone absorbs oxygen with gradual oxidation of chlorophyll. Wurmser (Arch. Phys. Biol. I, No. 3, Sept. 1921) has studied the photo-decomposition as a function of the wavelength of the light used. He found out that the amount of decomposition which takes place depends only on the amount of energy absorbed and is independent of the wavelength. He also concluded that the decomposition is an oxidation process. Chlorophyll is not so susceptible to photo-decomposition in the living leaf as it is in solutions in organic solvents. If water is added to an acetone solution of chlorophyll, a colloidal solution is formed and in this condition the stability of chlorophyll in presence of light is much increased. Wurmser found that addition of very small percentage of colloids such as casein, gelatine, albumin and gum arabic, made a solution of colloidal chlorophyll much more stable in presence of light. The addition of starch had practically no effect on the stability of chlorophyll. As a result of these experiments Wurmser suggested that the chlorophyll in the living leaf is probably protected against photo-decomposition and photo-oxidation by the presence of colloids. Albers (Phys. Rev. **46**, 1934, 336) has shown that the photo-decomposition of chlorophyll increases with increase of temperature. This would indicate that the photo-decomposition of chlorophyll is not entirely photochemical.

Knorr and Albers (Phys. Rev. **47**, 1935, 329) have shown that the fluorescence of chlorophyll vanishes as the solutions are bleached and that the chlorophylls and their derivatives decompose under

the action of light in acetone solutions and in an atmosphere of oxygen, carbon dioxide or nitrogen. The relative intensities of the individual absorption bands of chlorophyll change considerably during the photo-decomposition and photo-oxidation but the position of the bands does not shift. It is clear therefore that in the case of chlorophyll there is photo-decomposition as well as photo-oxidation in acetone and alcoholic solutions.

The experiments of Knorr with chlorophyll and its derivatives dissolved in acetone show that these are true cases of photo-decomposition and perhaps photo-reduction also by the reducing substance acetone because oxygen does not help the loss of fluorescence. From the above observations it is clear that chlorophyll occurring in the state of solution undergoes photo-decomposition, photo-oxidation and photo-reduction more readily than chlorophyll existing in the colloidal state or protected by colloidal substances like casein, gelatine or gum arabic. This conclusion is supported by the observations of Dhar and Bhattacharya (J. Indian Chem. Soc. 4, 1925, 299) on the bleaching of different dyes in air and sunlight aided by zinc oxide as a photo-catalyst. About forty dyes were investigated and the dyes can be classified according to their bleaching in three categories :—

1. Readily bleached :—Crystal violet, methylene blue, ethyl green, Nile blue, azolitmin, aniline blue, nigrosine, gentian violet, malachite green, methyl violet, eosin and fluorescein
2. Not readily bleached :—Indigo-caramine, rhodamine, erythrosine, uranine, acridine red, Congo red, aurine, magenta, aniline yellow, methyl orange, purpurin, tropeolin, aesculin, thioflavine.
3. Not bleached :—Alizarin blue, water blue, cupric blue, Victoria blue, pyronine, rose bengale, aniline red, auramine, aniline scarlet, theonine, corcus red, rosaniline, acridine orange and acridine yellow.

Among those which are easily bleached are chiefly the basic dyes and which exist generally in the dissolved condition and their

molecular weights are lower than those of acid dyes. The following basic dyes are not much bleached :—

Thioflavine, rosaniline, acridine orange, acridine yellow, auramine, magenta, acridine red, pyronine, aurine, rhodamine, erythrosine, victoria blue. Most of these dyes are partially colloidal in water.

The following are acid dyes and exist in colloidal state; these are not very much bleached :—

Alizarin blue, uranine, congo red, aniline red, aniline yellow, methyl orange, purpurin and tropeoline.

The aqueous solutions of substantive dyes tend to be colloidal while those of the non substantive dyes usually give molecular solutions. Benzopurpurin 4B a strongly substantive dye and the isomeric 4 : 4—diamino 2:2 toluidine analogue, a feebly substantive dye have been found by Robinson and Mill to have complex anions in solution, but those of the substantive dyes are much larger.

The adsorption of a dye by a fibre depends upon the size of the dye particle. If the particles are too small, i.e. if they approach the molecular dimensions the adsorption on the fibre is not much pronounced. On the other hand if the particles are too big, they may not form a uniform layer on the fibre. Hence particles resembling the precipitate condition or those in the dissolved conditions should not make good dyes. Particles of intermediate sizes should form better dyes. This view explains the usefulness of adding sodium salts in dyeing. It has been shown by Dhar and Chatterji (Koll. Z. 1925, **37**, 89) that various sols can be adsorbed by their freshly obtained precipitates. Similarly barium sulphate and other substances can act as adsorbents of colloidal matter. But such precipitates do not show much adsorption for substances in the molecular or ionic condition. It is clear, therefore, that the textile fibres can adsorb dyes in colloidal condition more than those in molecular condition.

Dhar and coworkers (J. Indian Chem. Soc. 6, 1929, 145) have determined the extinction coefficients and decolourisation, energetics

of the photochemical bleaching of Neocyanin (Kodak) by oxygen of air. This colouring matter shows marked light absorption in the red and infra-red side and the velocity of the photochemical bleaching is largest in the regions 3704° A and 8500° A where the light absorption is also maximum. The bleaching is proportional to the square root of the changes in light intensity and the temperature coefficient of bleaching varies from 1.04 to 1.30 and the quantum efficiency changes from 1 to 4 depending upon the wavelength of light.

The bleaching of very dilute solutions of Dicyanin by oxygen of the air in light was also investigated by Dhar and Mukerji (*J. Phys. Chem.* **33**, 1929, 850) The reaction is unimolecular and the temperature coefficient is about unity and the quantum yield varies from 0.5 to 2.0.

The bleaching of Chinaldin cyanin, pinachrome cyanin, lepidin-cyanin, Pinaverdol in collodion films was investigated by Lasareff (*Ann. Physik* **24**, 1907, 661) and the bleaching has been attributed to the oxidation of the dye by oxygen. From the data of Lasareff, Bodenstein (*ibid.* **37**, 1912, 812) concluded that the quantum yield is much smaller than unity. Apart from this photo-oxidation there is a photo-chemical decomposition of the dye, as well as an interaction of the nitro cellulose of the collodion and the dye in presence of light. The temperature coefficient of the reaction is almost unity.

Waviloff (*Z. physik. Chem* **100**, 1922, 266) studied the bleaching of pinaverdol, cyanine, lepidine cyanin and chinaldincyanin in the dark between 60° and 120° in collodion film. It seems that a reaction takes place between the nitro-cellulose and the dyes at this high temperature. There is no bleaching of the solid dye at this temperature interval in the absence of collodion. The temperature coefficient in the thermal process is two.

Weigert (*Z. Physik* **5**, 1920, 410), Predwoditeff and Netschajewa (*ibid* **32**, 1925, 226) observed that the initial rate of bleaching of these dyes in collodion films on illumination is proportional to the light absorbed when the concentration of the dye is very small. When the concentration of the dye is increased the velocity becomes a periodic function of the dye concentration.

Zchodro (*J. chim. phys.* 29, 1929, 59) has shown that the electric conductivity of the collodion films coloured with cyanin, pinaverdol or pinachrome increases on illumination but no increase is observed when the film has become decolourised. When illumination ceases the electric conductivity gradually decreases.

Chemiluminescence in the oxidation of dyes.

The glow observed when different dyes and organic substances are oxidised by ozone or hydrogen peroxide has been investigated by Dhar and coworkers (*Z. anorg. Chem.* 173, 1928, 125) with the following results :—

Dyes.	Solvent.	wavelength of light emitted
Eosin	Methyl alcohol	6020 to 5320 °A.
Uranine	Ethyl alcohol	5860 to 5030 „
Neutral red	Methyl alcohol	6050 to 4850 „
Rhodamine B	Ethyl alcohol	6170 to 4670 „
Thioflavine	Ethyl alcohol	5700 to 4690 „
Cartharamine	Methyl alcohol	6650 to 4580 „
Rhodamine BJNN	Ethyl alcohol	6190 to 4620 „
Erythrosin	Ethyl alcohol	6060 to 5310 „
Cartharamine	Ethyl alcohol	6050 to 5860 „
Rhodamine	Ethyl alcohol	5910 to 5530 „

The foregoing fluorescent dyes gave out the best glow amongst the numerous dyes investigated by us. When ozonised oxygen is passed through solutions of the following fluorescent and non-fluorescent substances a glow is also observed but the intensity of the glow is less than that obtained with the first group of fluorescent dyes :—

Methyl blue, alizarin, resorcinol benzene, azure eosin, rose bengale, theonine, methylene blue 2B, chlorophyll, resorcinol succinyl, resorcinolacetonedicarboxylene, gallein, fluorescein alkaline and aesculin.

There are several other dyes in which the glow was less intense than in the two previous groups. We have also observed that several dyes, when oxidised by hydrogen peroxide and ferrous sulphate become luminous. In this case both fluorescent and non-fluorescent dyes when oxidised by hydrogen peroxide and ferrous sulphate give out glow.

It is interesting to note that the glow on the oxidation of dyes is intense when the dyes are fluorescent. The chemiluminescence spectra of Rhodamine B extends from 6170 to 4670°A. and the fluorescent spectrum recorded by Kautsky and Neitzke (*Z. Physik.* **31**, 1925, 60) consists of lines from 6680 to 4400°A. Hence it appears that the chemiluminescence spectra and fluorescent spectra of Rhodamine B are not altogether identical as has been assumed by Kautsky. Numerous fluorescent and non-fluorescent substances give out glow when oxidised by ozonised oxygen or hydrogen peroxide and ferrous sulphate and the glow is intensified by warming the solutions. But the view advanced by Jorissen (*Chem. Weekbend* **1**, 1904, 789) and Moureu and Dufraisse (Reports of Solvay international council of chemistry Brussels, 1925, page 524) that slow oxidation is always accompanied by luminescence is not correct because there are numerous substances which can be oxidised either by oxygen or hydrogen peroxide or ozone and do not emit a glow. The intensity of the glow given out in the oxidation of dyes becomes less with the increase in the concentration of the dye. The late Professor J. Perrin reported (*Ann. d. Phys.* (9) **10**, 133, 1918) *Compt. rend* **177**, (1923, 714) that the intensity of fluorescence of substances decreases considerably as the solution is concentrated. He also advanced the view (*ibid.* **178**, 1924, 1401) that the phenomenon of fluorescence is caused by the decomposition of the molecules of the fluorescent substances. In other words Perrin included fluorescence in the domain of chemiluminescence.

Wood (*Phil. Mag.* (6), **43**, 1922, 757) supported the hypothesis of Perrin from his experiments on rhodamine.

It is observed that an aqueous solution of aesculin in contact with the atmosphere loses about 60 per cent of its fluorescing power when exposed in a glass tube to the radiations of a mercury arc for one hour. The active wavelengths are longer than 3300°A . in this case. In an evacuated glass tube the fluorescence power remains constant during an irradiation period of 30 hours. In a quartz tube evacuated and sealed off, the intensity of the fluorescence decreases after 2 hours to 19 per cent of its initial value. This loss is due to the photo-decomposition of aesculin by the absorption of the mercury lines of wavelengths below 3300°A . As a general rule it can be stated that the organic and inorganic fluorescent materials are much less subjected to fading if they are carefully protected from oxygen and in some cases from water vapour.

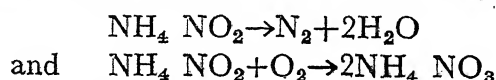
It is generally found that the closed ring structure of the dye is associated with the appearance of fluorescence. Only 85 out of the 1450 dyestuffs listed in the colour index give out fluorescent light. None of the large group of dyes included in the azo dyestuffs is fluorescent. The most brilliantly fluorescent compounds fluorescein, eosin and rhodamine belong to the xanthene group. Euchrysine, trypanflavine, choriphosphine in the acridine group, primulin and thioflavine in the thiazole group, magdala red and safranin in the azine group and some indanthrene dyes show marked fluorescence and they all contain a closed ring structure. On the other hand, the open bridge compounds like auramine, malachite green or crystal violet are not fluorescent.

It seems that although the closed ring structure adds more stability towards photo-chemical oxidation of the dyes than the open chain compounds like malachite green but the fluorescent dyes are liable to be photo-chemically oxidised by oxygen of the air and in this respect they behave like chlorophyll.

Weigert (*Z. Physik.* **10**, 1922, 349), McLennan and Miss Cale (*Proc. Roy. Soc.* **102 A**, 1922, 256) Miss Kearney (*Phil. Mag.* **47**,

124,48) Pringsheim (*Z. Physik* **10**, (1922), 176) and Chakravarti and Dhar (*Z. anorg. Chem.* **142**, 1925, 299) and Beese and Marden (*J. optical Soc. Am.* **32** (1942), 317) showed that the bleaching of fluorescent substances is not caused by fluorescence but is due to the photo-oxidation of the organic compounds by oxygen of the air. Hence the bleaching of the dyes on exposure to light is in most cases due to photo-oxidation and in some cases when the illumination is intense the photo-decomposition of dye can take place. This phenomenon of fading has nothing to do with the fluorescence of substances.

We have shown that the solutions of ammonium nitrite, when exposed to light and air in the presence or absence of substances like silica, zinc oxide or titanium dioxide undergo two types of changes, photo decomposition and photo oxidation according to the equations;



Many dyes also can undergo photo-oxidation and photo-decomposition like ammonium nitrite, the difference being that in the case of ammonium nitrite the photo-decomposition is more pronounced than the photo-oxidation, while with the dyes photo-oxidation is more pronounced, specially with basic dyes, than photo-decomposition. It is clear, therefore, that the phenomenon of fluorescence of colouring matter cannot be included in the realm of chemiluminescence.

Dyes as Photo-sensitizers and Desensitizers.

In 1873 Vogel discovered accidentally that photographic plates stained with a yellow dye showed a maximum sensitivity to light in green instead of the blue region of the spectrum. Becquerel in 1874 found that chlorophyll had the same effect. In 1875 Water-house observed that eosin is a powerful sensitizer for green and yellow light. The associated dyes rose bengal and erythrosin are still used for this purpose.

It is well known that at present colouring matters are extensively used in increasing the sensitivity of photographic plates. It has been observed that a maximum of sensitiveness corresponds to a maximum

light absorption. The photographic plates become sensitive to the rays absorbed by colouring matters. But all coloured substances cannot act as optical sensitizers. In order that a coloured substance may be active, it is necessary that it should be absorbed by the silver halide and must be able to exert a reducing action on the silver salt. Among the substances possessing an optical sensitizing power the following are important:—

For the greenish blue—Chrysaniline, acridine yellow, uranine.

For the yellowish green—Eosin, erythrosin, quinoline red.

For the orange—Cyanine, methyl violet.

For the orange red—Nigrosine, pinacyanol.

For the red and infra-red—Dicyanin, Neocyanin, Kryptocyanine

All these substances do not have the same importance. Eosin and erythrosin which show the maximum of absorption in the yellow green part of the spectrum are very convenient for the purpose of sensitization to visible light. Cyanine which absorbs specially in the orange increases the sensitiveness to red light better than eosin, but it has a tendency to fog the plates as it exerts a marked reducing action on the silver halide and hence is seldom used without mixing it with other sensitizers. Most of these sensitizers are basic dyes containing iodine and can act as reducing agents specially in presence of light. Hence they perform dual functions, i.e., marked absorption of visible light which helps in the decomposition of silver halide, and photo-reduction of the silver halide. Both these functions are prominent in the phenomenon of photo-sensitization. The colouring matters of leaves chlorophyll-a $C_{55}H_{72}O_5N_4Mg$, chlorophyll-b $C_{55}H_{70}O_6N_4Mg$, xanthophyll $C_{40}H_{56}O_2$ and carotin $C_{40}H_{56}$, not only absorb visible light markedly but also being reducing agents exert reducing action on the carbonic acid and help in carbohydrate production.

For colour photography by the Lumiere process, it is necessary that the emulsion should possess as uniform a sensitiveness as possible to all parts of the spectrum. Panchromatic plates can be obtained

by sensitizing the ordinary plates with orthochrome-T or ethyl red, both of which possess two maxima of absorption, one in the green and the other in the yellow.

The blue lepidine cyanines extend the sensitivity into the red. Orthochrome-T (p-toluquinaldin-p-toluquinoline ethyl cyanine) gives a very uniform sensitization, whilst pinachrome (p-ethoxy quinaldine p-ethoxy quinoline ethyl cyanine) sensitizes upto 6500°A . pinaverdol (p-toluquinaldine quinoline methyl cyanine) is particularly effective in the green and yellow. True panchromatic sensitivity is obtainable with pinacyanol and ethyl cyanine, both being effective in 6000°A . Dicyanin and neocyanine are useful right upto the extreme limit of visible red and the near infra-red, without causing undue predominance at the other end of the visible spectrum. 'Homocol' and 'Isocol' produced by the Baeyer company are of this type. Kryptocyanin acts as a good sensitizer for the near infra red rays. It is efficacious upto 8500°A . and dicyanin even beyond 9000°A . One of the carbocyanines Xenocyanin gives a maximum sensitivity at 9660°A . and extends upto 13500°A .

Pinaverdol and Orthochrome-T are generally very rapidly decolourised on exposure to light in aqueous solutions or thin films and they are basic dyes. They can be applied to tanned cotton but are mainly used for sensitizing photographic plates towards green light.

The isocyanines are reddish purple dyes but too costly and fugitive to be of value for application to fabrics. They sensitize photographic plates upto the orange. The most even and rapid sensitization is caused by the methyl compounds and this action becomes less pronounced when larger alkyl groups are used as substitute. This shows clearly that light sensitiveness generally decreases with increasing molecular weight. Amongst the isocyanin compounds the most valuable ones are ethyl red, sensitol green or pinaverdol. The carbocyanines sensitize photographic plates in the yellow red parts of the spectrum and are more active than isocyanines. Unlike the corres-

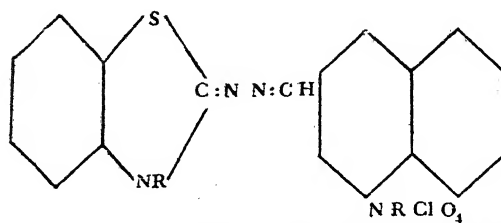
ponding isocyanines, the methyl carbocyanines are poor sensitizers. The ethyl derivatives are the best and the higher alkyl derivatives fall off in value as the series is ascended. This shows again that an increase in the molecular weight makes the dye more stable. The most valuable substance of this class is Pinacyanol or sensitol red which is 1 : 1 diethyl 2 : 2 carbocyanine iodide.

The thiocarbocyanines are bluish red or purple dyes. They can be applied to tanned cotton but are mainly notable for their powerful sensitizing action on the photographic plate. Similarly oxacarbothiocyanines with oxygen in place of sulphur have also been obtained and used as photo-sensitizers.

The indocarbothiocyanines, notably Indolenine red is a pure and coloured dye fast to acid and alkali but only moderately fast to light. In its dyeing properties it resembles Rhodamines. The Apocyanines constitute an exceptional class of substances in which two quinoline nuclei are directly combined. Recently carbocyanine dyes have been prepared with larger polymethine chains containing two heterocyclic nuclei. These include the dicarbocyanine with a connecting chain $\text{CH} : \text{CH} \text{ C Br} : \text{CH} \cdot \text{CH}$ and the tricarbocyanines. The absorption spectra maximum and the production of maximum photographic sensitivity are both nearer to red end of the spectrum than in those of the corresponding simple carbocyanines.

The cyanine dyes including isocyanine, carbocyanine, thiocarbocyanines, indocarbo-cyanines, oxacarbo-cyanines, apocyanines have been largely used as photographic sensitizers. The best known amongst them have already been named. All these substances are rich in carbon and hydrogen and do not contain any oxygen but are usually iodo-derivatives. Apparently they behave as reducing agents and are likely to be unstable like iodoform and undergo photo-oxidation by air. Hence they are suitable as sensitizers and act as great absorbers of light and exert reducing action on the silver halide of the photographic plate. Similarly Rose Bengale, eosin, erythrosin also act as photo-sensitizers, for although they contain oxygen, they are rich in carbon and hydrogen and thus exert reducing action on the silver salt.

Aurantia which contains six nitro groups can act as a photographic desensitizer. Being an unstable substance it can undergo decomposition in light and is not reducing in its properties like photosensitizers. The following substance has also been found to be a desensitizer.



3 : 1 Dialkyl 8 : 9 diazothia-2 carbocyanin perchlorate.

The function of the desensitizer appears to be as follows :—

The light energy absorbed by the desensitizer is dissipated as soon as possible without reacting on the silver halide molecule. The desensitizer forms a stable adsorption complex and probably completely covers the silver halide molecule and does not exert any reducing action on the same.

In case of Aurantia, the desensitizing effect may be due to the absorption of light by the molecules and their consequent decomposition, thus the absorbed light is completely dissipated without affecting the photographic emulsion. The action of other desensitizing agents may be explained in the same way. In some cases, however, the light absorbed by the dye is converted into heat immediately. Phenosafranine has been used as a desensitizer for a long time ; it can markedly absorb visible light and is not a reducing agent. Just as a large number of NO_2 groups present in a dye make it unstable, similarly a large number of iodine atoms in a molecule is likely to make a dye also unstable. It seems, therefore, that such iodo compounds after absorbing light can break up and thus dissipate the light energy absorbed and should be able to act as desensitizers. Similarly the perchlorate 3 : 1 dialkyl 8 : 9 diazothia 2 carbocyanin perchlorate may be unstable like Aurantia and may break up by light absorption.

The preparation of cyanin dyes containing nuclei other than the original one, i.e., quinoline, greatly enlarges the field of this group of dyes as did observations that the new type of cyanines had valuable photographic properties. The cyanine dyes of long chains have made possible the preparation of infra-red sensitive photographic materials which are used for long distance photography and also for their power of conferring sensitivity to light of various colours. This has made possible a true rendering of colours in monochrome and led to a great increase in speed, specially to artificial light. The high achievements of modern photography are, in fact, largely due to photographic sensitizers of which cyanines are amongst the most important. Sensitizers have also made possible the technicolour photography.

Isocyanines have appeared in the market under the names, ethyl red, Homocol, Isocol, orthochrome-T, pericol, pinachrome, pinachrom violet, pinaverdol and sensitol green; whilst cyanines are marketed under the names of ethyl cyanin-T and quinoline blue.

Fuchs (*Chem. Ztg.* **57**, 1933, 853) pointed out that certain sensitizers containing benzthiozole nuclei are superior to the older cyanines in that, they inhibit chemical fog because they are less reducing in their action on the silver halide. This is also confirmed by Sobolev, Bondareva and Evteeva (*J. Appl. Chem. Russia*, **9**, 1936, 335) who compared the sensitizing action of various substituted cyanines containing benz and naphtha-thiozole nuclei. With complex compounds of tungstic or molybdic acid, the indocyanines and indocarbocyanines give coloured lakes which are fast to light.

The I. G. Farben Industries state that indoxyl carbocyanines are specially good photo-sensitizers.

Beattie, Heilbron and Irving (*J. Chem. Soc.* 260, 1932) found that whilst the halogeno-carbocyanines are sensitizers for the deep red or the near infra-red, the corresponding nitro-dicarbocyanines possess desensitizing properties.

The neo cyanines sensitize into the deep infra-red. The azocyanines are dyes with colours varying from yellow to deep red in solution and can act as photographic desensitizers. According to Brooker and

Keys (*J. Franklin Ins.* **210**, 1935, 255) the furthest photographic excursions into the infra-red have been made possible by the discovery of long chain tetra- and penta-carbocyanines. On comparing the cyanine dyes, the paradimethyl aminobenzyl-benzylidin, quinaldine ethi-iodide and paradimethyl amino anil of quinaldialdine aldehyde ethi-iodide on one hand and on the other hand paradimethyl amino-benzaldine- β naphtha quinaldine ethi-iodide and the paradimethyl amino anil of β -naphtha-quinaldine aldehyde-ethi-iodide, it is found that the replacement of : CH by : N had the effect of broadening the absorption band, decreasing its intensity and shifting it towards the red. If the linking is by a : CH group, which is reducing in its action, the dye is a photographic sensitizer, but if replaced by a nitrogen atom it possesses desensitizing properties. This appears to be a general rule. It is clear, therefore, that both photographic sensitizers and desensitizers must possess strong light absorption power. But the sensitizer is much more reducing in its action.

It is well known that the ordinary photographic plate is not sensitive to ultra-violet light of radiations shorter than 2200° A. and this has been attributed to the absorption of the incident radiation by gelatine.

Schumann (*Ann. der Physik.* **5**, 1901, 349) showed that plates made with as little gelatine as possible were sensitive to radiations of wavelength 1250 to 2200° A. It is clear, therefore, that in ordinary photographic plates, short ultra-violet light is completely absorbed before it can reach the silver halide. These observations throw considerable light on the functions of photographic desensitizers which like gelatine actually absorb the whole of the incident light before it can reach the silver halide. All desensitizers must be capable of absorbing the incident radiations almost as completely as possible, so that none of the incident radiations can penetrate and affect the silver halide on the photographic plate.

The fogging action of some sensitizers on photographic plate is chiefly due to the reducing action of the sensitizer on the silver halides. All sensitizers which are readily bleached by absorption of oxygen in

presence of light are the ones which generally fog the photographic plates.

In this connection the observations of Padoa and Mervini (*Atti. R. Acad. Lincei*. **25**, 1916, 168) showing that the action of hydroquinone in developing photographic plates is not only accelerated at higher temperatures but the silver bromide which has not been affected by light is also reduced and the plate becomes foggy, are of great interest.

It has been already stated that basic dyes are more reducing in properties than acid dyes and are less fast than the acid dyes. Moreover more basic dyes are used as photosensitizers than acid dyes because basic dyes not only absorb light but also reduce the silver halide specially in light. These observations are supported by the results obtained by Schmidt (*Z. Wiss. Phot.* **26**, 1928, 86) who has reported that with photographic plates sensitized with basic dyes, there is more marked reduction in the sensitivity than with acid dyes, when the plates are treated with potassium chromate and sulphuric acid; the reason is that the basic dyes absorbed by the silver halide are more readily oxidised by the chromic acid than are the acid dyes which are less reducing in their properties.

The tetra- and penta carbocyanines are excellent photo-sensitizers but are unstable dyes and the stability decreases as the chain is elongated.

Because of the very great importance of cyanine dyes in photo-sensitization and desensitization numerous complex cyanine dyes including isocyanines, thiacyanines, thiocarbocyanines, symmetrical and unsymmetrical carbocyanines, oxacyanines, oxacarbocyanines, selenacyanines, selenacarbocyanines, thiazolecyanines, thiazole carbocyanines, oxazole cyanines, selenazolocyanines, thiazolino carbocyanines, neocyanines, apocyanines, azacyanines, etc. have been prepared and their properties studied with great vigour in many countries.

The great increase in speed of panchromatic emulsions witnessed in recent years has been largely due to the new technique of 'super sensitization'. That it is possible to attain sensitization by the addi-

tion of such super sensitizers greater than the sum total of the individual sensitizers, is claimed by C. E. K. Mees. An alcoholic solution of the sensitizer and the super sensitizer is diluted with water and added to the emulsion. As for instance, ten parts of pinacyanol may be super sensitized with one part of pinaflavol, the region of response induced by each overlapping. The net effect is to obtain greater speed in sensitized region than the sum of the two sensitivities conferred by each separately. Another example is that of a thiocarbocyanin, super sensitized by the addition of 8—alkyl diabenz-thiocarbocyanin. It seems that in such cases the light absorption by the mixture is greater than the absorptions of the two sensitizers estimated separately (Compare Dhar and co-workers *J. Indian Chem. Soc.* **11**, 33, 311, 629 (1934), **17**, 673 (1940).

The amount of these sensitizers added to an emulsion is small as compared with fluorescein salts. About 0.05 per cent of the weight of silver bromide would be used in the case of pinacynol; 0.07, per cent in the case of pinachrome, orthochrome-T or pinaverdol. These dyes absorb light very markedly and are all rapidly decolourised on exposure to light in form of aqueous solutions or thin films.

SUMMARY.

1. Basic colouring matters usually contain large number of carbon and hydrogen atoms and behave as weak reducing agents and are oxidised by the oxygen of the air, specially in presence of light and thus become light fugitive.
2. Acidic dyes are richer in oxygen than the basic dyes and are not oxidized by atmospheric oxygen as much as the basic dyes.
3. In general basic dyes have smaller molecular weights than acidic dyes. The greater the molecular weight of a dye, the greater is its stability towards photo-oxidation.
4. The acidic dyes exist when mixed with water mostly either as finely divided particles insoluble in water or colloidal aggregates. The basic dyes usually exist in the molecular condition when dissolved in water.
5. The naturally occurring colouring matters contain more oxygen than the artificial basic dyes and resist photo-oxidation specially when they are in the colloidal condition or protected by other colloids.

6. When fluorescent and non-fluorescent colouring matters in alcoholic and aqueous solutions are oxidized by ozone or hydrogen-peroxide and ferrous sulphate, a glow is observed. The glow is more pronounced with fluorescent colouring substances. The bleaching of fluorescent colouring matters is not caused by their fluorescence but is due to their photo-oxidation or photo-decomposition.

7. A colouring matter can fade due to (1) photo-decomposition, (2) photo-oxidation by air, (3) photo-reduction by the fibre or the mordant.

8. Photo-sensitisers play a very important part in modern photography. The colouring matters used as photo-sensitizer perform dual functions, i.e., act as a marked absorbent of visible light and exert reducing action on the silver halide. Photo-sensitizers are usually basic dyes.

9. Photographic desensitizers are also good absorbents of light but cannot exert reducing action on the silver halide. The desensitizing effect is chiefly due to the complete absorption of light by the desensitizing colouring matter. Thus the light cannot reach and affect the silver halide. In the case of some desensitizers the absorbed light breaks up the desensitizer molecules and is completely dissipated before it reaches the silver halide particles.

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